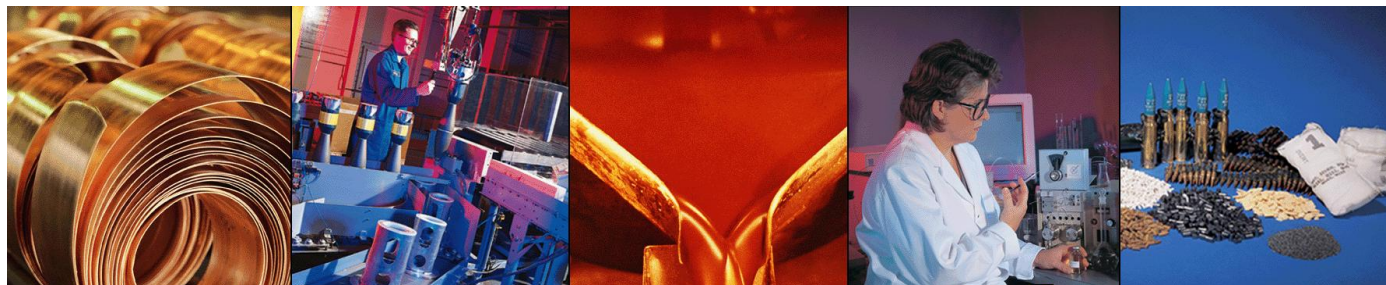


GENERAL DYNAMICS

Ordnance and Tactical Systems–Canada Valleyfield



Cellulose specifications: Summary of the 2009 proposed up-upgrades and improvements and new possibilities for future revisions

*7th International Nitrocellulose Symposium
Montreal, Canada
June 2016*

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³ *Consultant; former U.S. DoD, PEO-Ammo, PM-CAS, Picatinny Arsenal, NJ, USA*

This the presentation is divided in 6 sections:

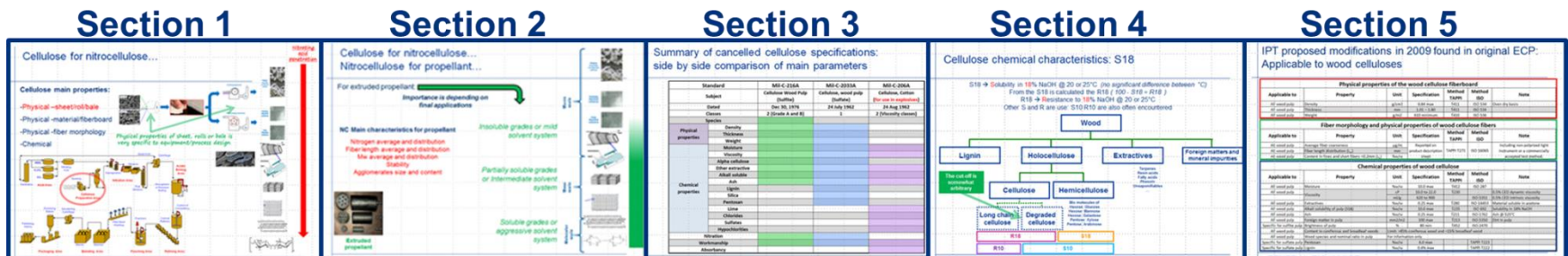
Section 1 and 2: The path from cellulose to nitrocellulose and to propellant

Section 3: Review the three canceled specifications and differences between them.

Section 4: Review of the chemical characteristics. In the past, was central in specifications. Ideally, two other sections would be required: physical characteristic of the fiberboard and physical characteristics of the fiber.

Section 5: Review the 2009 IPT's proposed modifications as presented in original ECP.

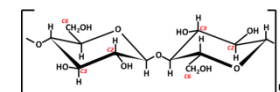
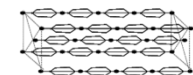
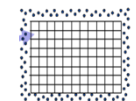
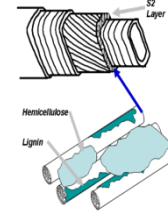
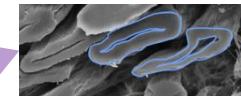
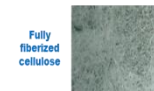
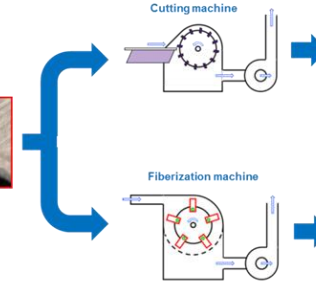
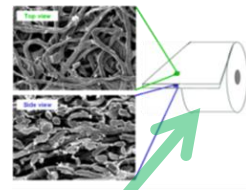
Section 6: On the complexity of changing a specification



Cellulose for nitrocellulose...

Cellulose main properties:

- Physical –sheet/roll/bale (and workmanship)
- Physical -material/fiberboard
- Physical -fiber morphology
- Chemical

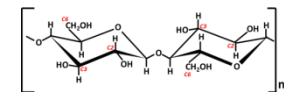
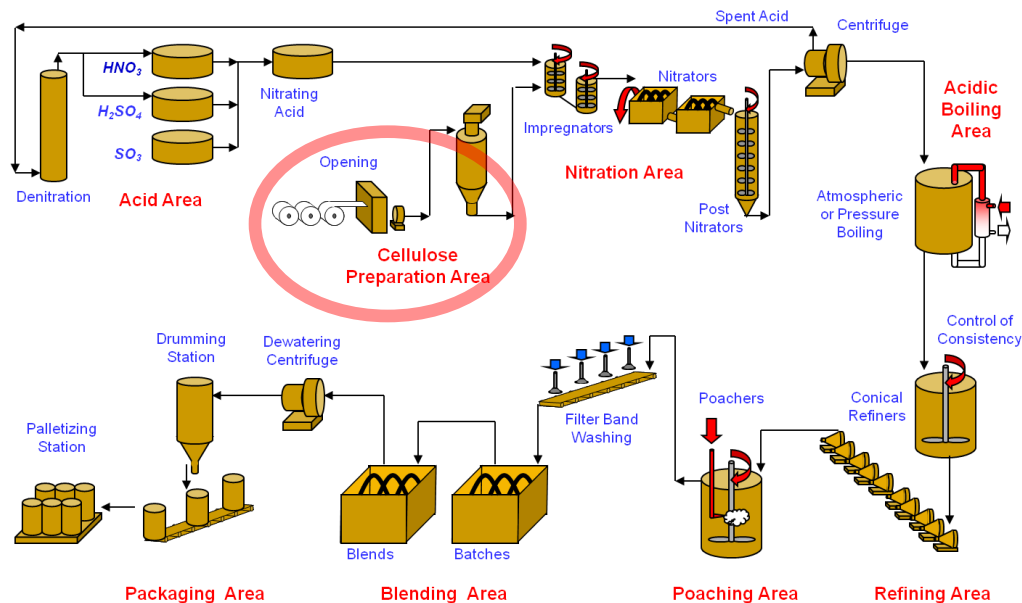


Nitrating
acid
penetration



**Nitrating
acid
penetration**

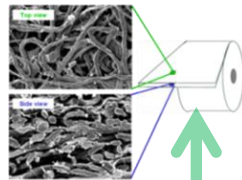
Physical properties of sheet, rolls or bale is very specific to equipment/process design



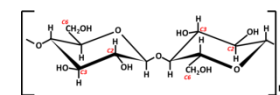
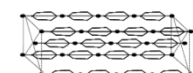
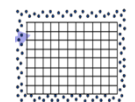
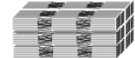
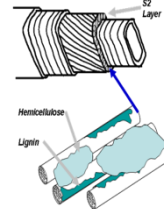
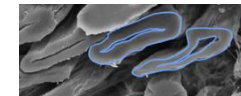
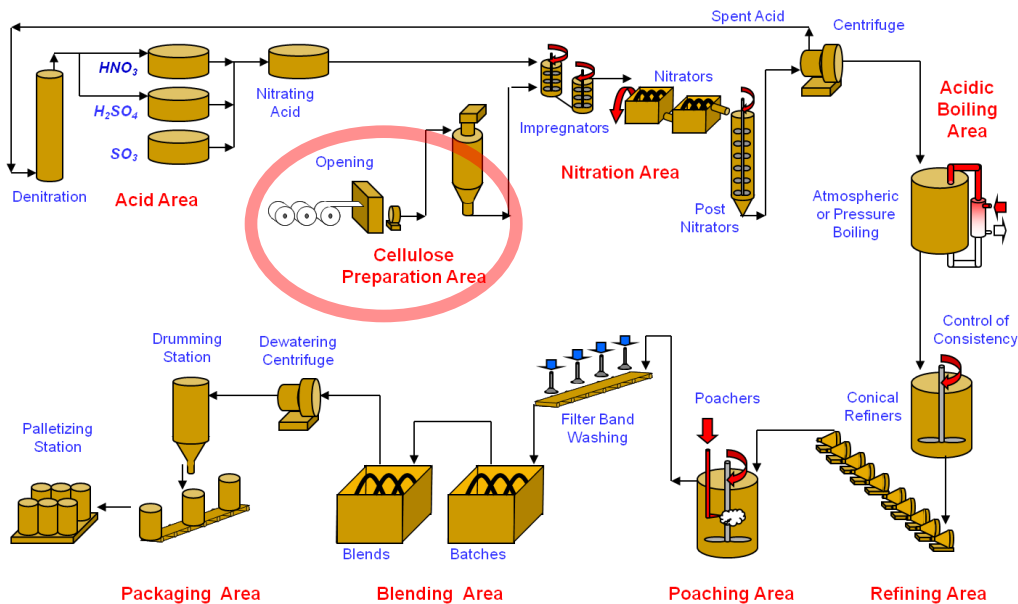
Cellulose for nitrocellulose...

Cellulose main properties:

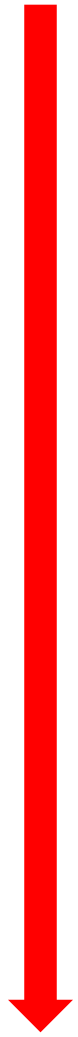
- Physical –workmanship
- Physical -material/fiberboard
- Physical -fiber morphology
- Chemical



Not specific to equipment/process design



Nitrating acid penetration

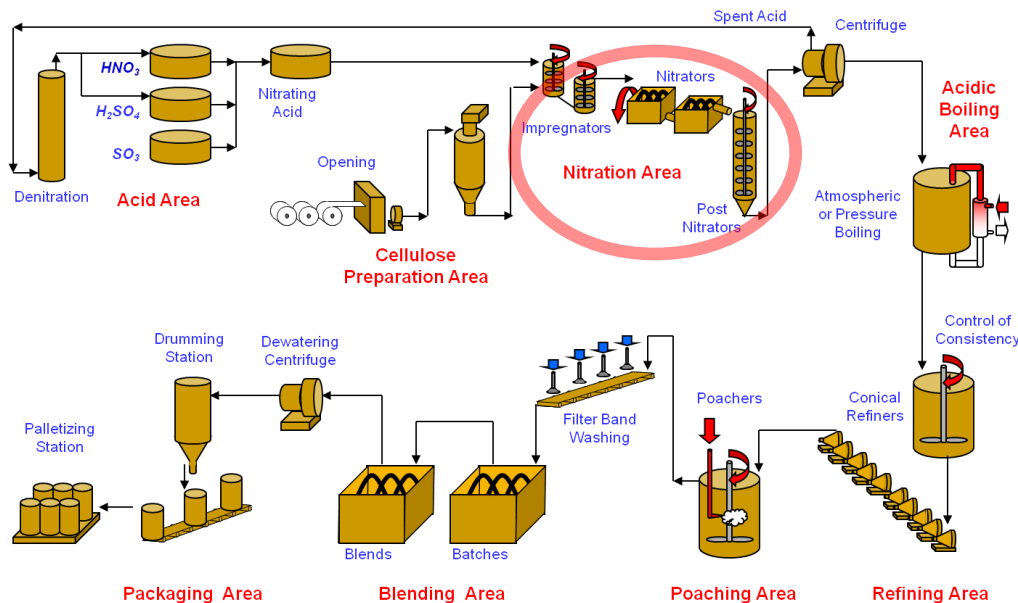
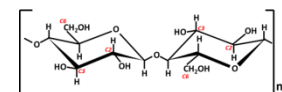
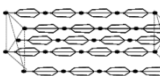
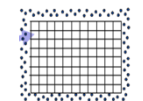
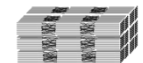
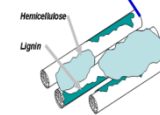
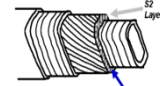
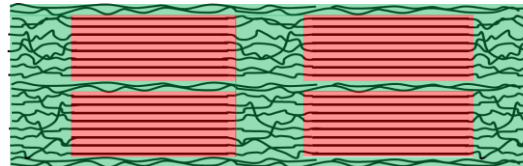


Cellulose for nitrocellulose...

Cellulose main properties:

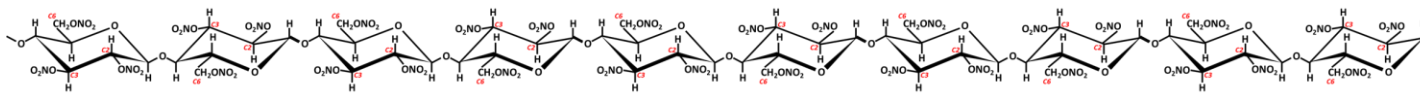
- Physical –sheet/roll/bale
- Physical -material/fiberboard
- Physical -fiber morphology
- Chemical

The nitration quality is mainly affected by diffusivity of nitrating acid into the cellulose matrix.



Nitrating acid penetration



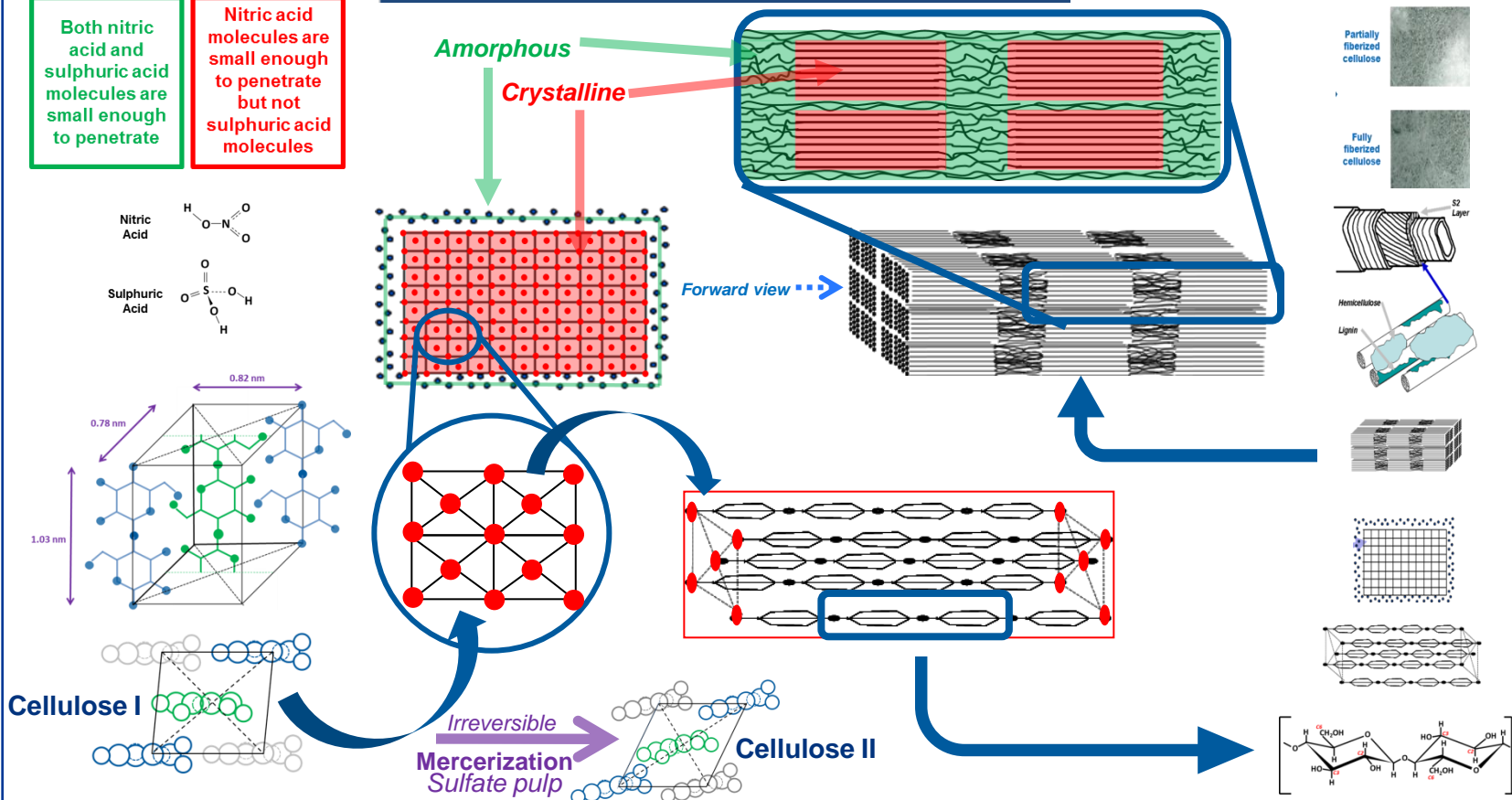


Nitrating
acid
penetration

Nitrogen variations within a NC molecule

Amorphous zone	Crystalline zone
Both nitric acid and sulphuric acid molecules are small enough to penetrate	Nitric acid molecules are small enough to penetrate but not sulphuric acid molecules

Typical	% Crystallinity	% Amorphous	% Accessibility
For wood:	60%	40%	60%
For cotton	70%	30%	50%

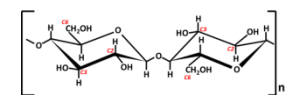
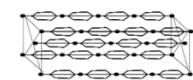
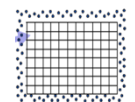
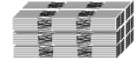
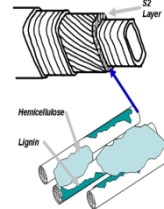
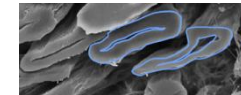
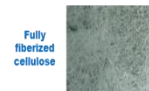
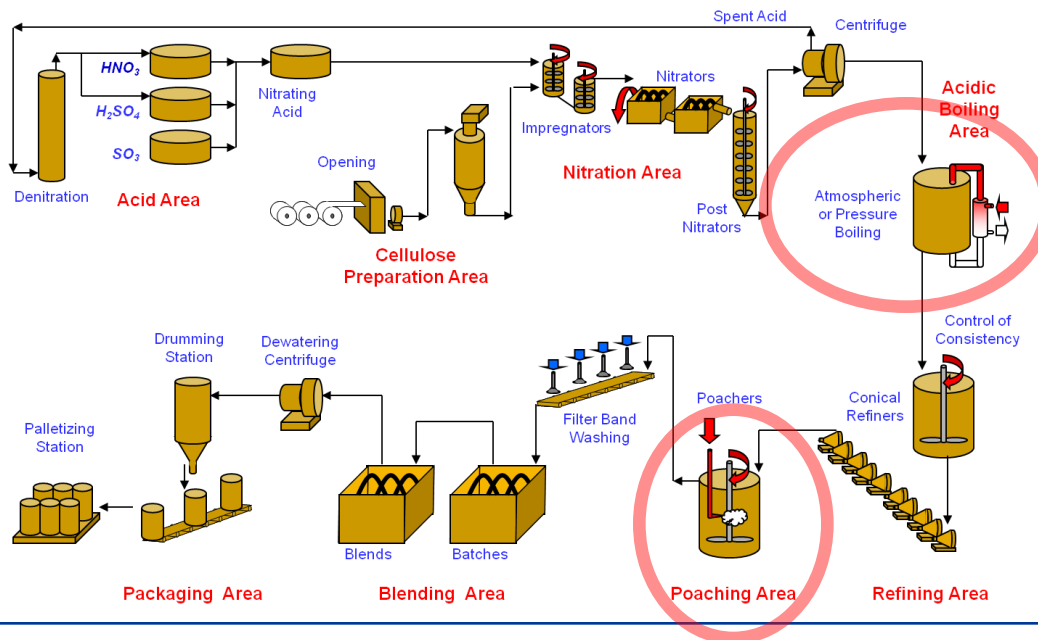


Cellulose for nitrocellulose...

Cellulose main properties:

- Physical –sheet/roll/bale
- Physical -material/fiberboard
- Physical -fiber morphology
- Chemical

The stabilization and depolymerization of NC is affected by the chemical purity and original Mw

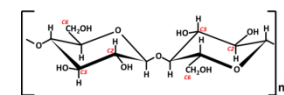
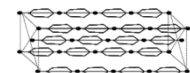
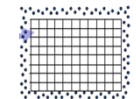
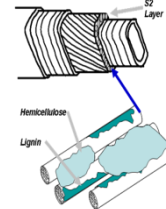
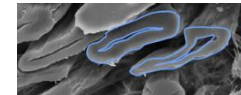
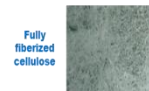
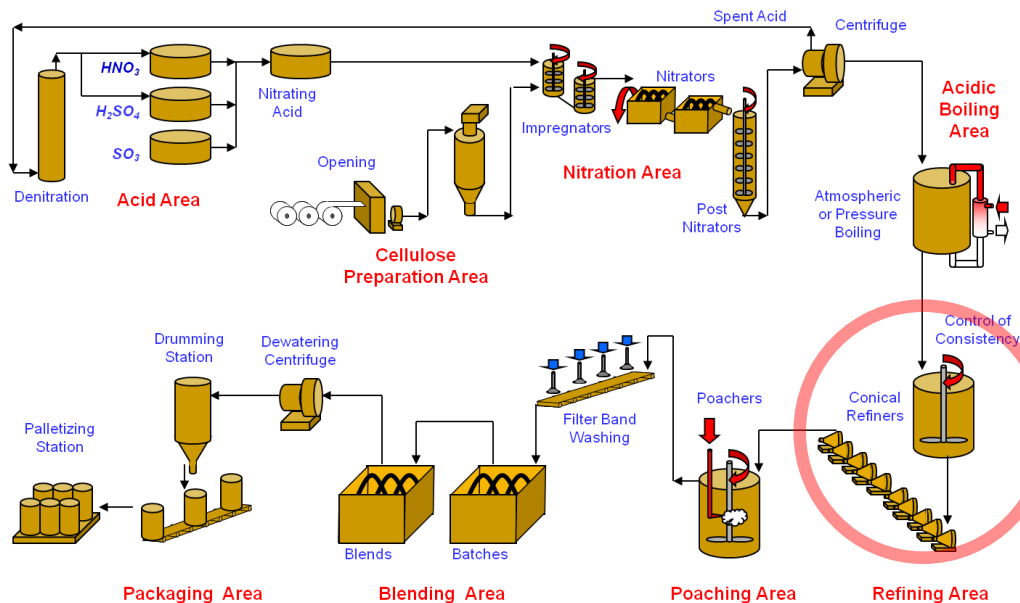


Cellulose for nitrocellulose...

Cellulose main properties:

- Physical –sheet/roll/bale
- Physical -material/fiberboard
- Physical -fiber morphology
- Chemical

The refining to proper length average and distribution of NC is affected by the physical characteristics of the fibers and the density of original fiberboard

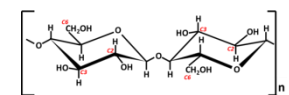
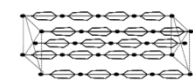
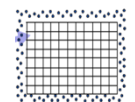
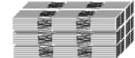
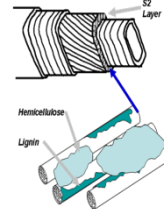
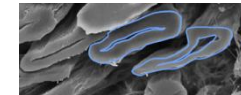
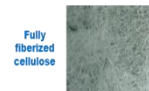
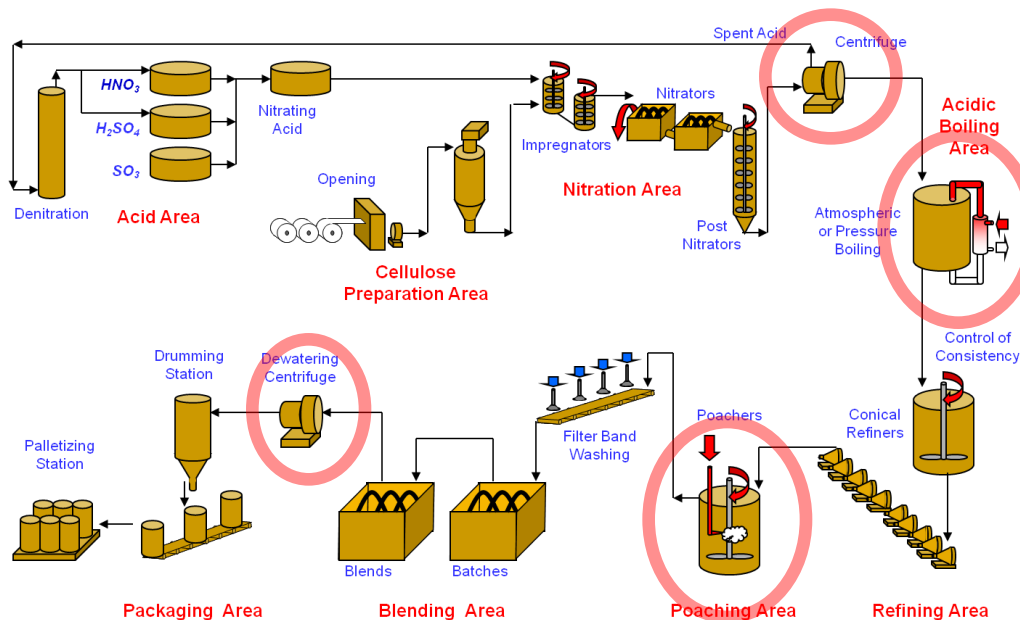


Cellulose for nitrocellulose...

Cellulose main properties:

- Physical –sheet/roll/bale
- Physical -material/fiberboard
- Physical -fiber morphology
- Chemical

The ability to drain liquid rapidly is important for NC. This is mainly affected by physical characteristics of the pulp.



Cellulose for nitrocellulose...

Nitrocellulose for propellant...

For spherical propellant:



Totally soluble applications

NC Main characteristics for propellant

Nitrogen content average and distribution

Fiber length average and distribution

Mw average and distribution

Stability

Agglomerates size and content



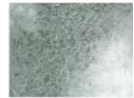
**Spherical
propellant**

Macro
scale

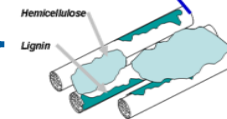
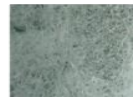
Flakes
Essentially
non-fiberized
cellulose



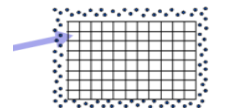
Partially
fiberized
cellulose



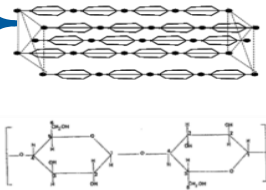
Fully
fiberized
cellulose



Meso
scale



Molecular
scale



Cellulose for nitrocellulose...

Nitrocellulose for propellant...

For combustible cartridge case:



NC Main characteristics for propellant

- Nitrogen content average and distribution
- Fiber length average and distribution
- Mw average and distribution
- Stability
- Agglomerates size and content



Combustible cases

Totally insoluble applications

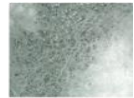
Fiberization quality and fiber characteristics

Macro scale

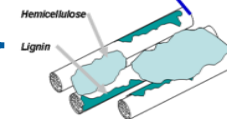
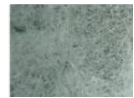
Flakes
Essentially non-fiberized cellulose



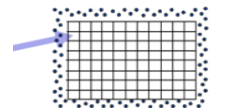
Partially fiberized cellulose



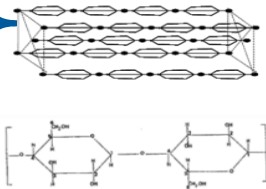
Fully fiberized cellulose



Meso scale



Molecular scale



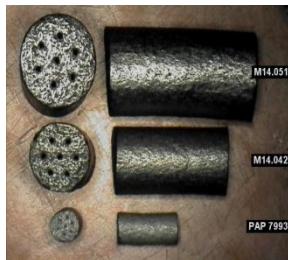
Cellulose for nitrocellulose... Nitrocellulose for propellant...

For extruded propellant:

Importance depends on final applications

NC Main characteristics for propellant

Nitrogen content average and distribution
Fiber length average and distribution
Mw average and distribution
Stability
Agglomerates size and content



Extruded propellant

Insoluble grades or mild solvent system

Partially soluble grades or Intermediate solvent system

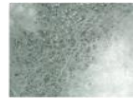
Soluble grades or aggressive solvent system

Macro scale

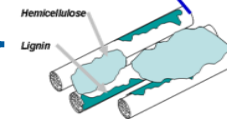
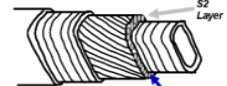
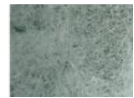
Flakes
Essentially non-fiberized cellulose



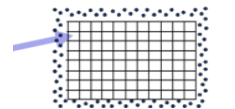
Partially fiberized cellulose



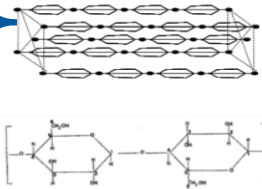
Fully fiberized cellulose



Meso scale



Molecular scale



Summary of canceled cellulose specifications

Most of these methods are really out of date

Standard			Mil-C-216A				Mil-C-2033A	Mil-C-206A	
Subject			Cellulose Wood Pulp (Sulfite)				Cellulose, wood pulp (Sulfate)	Cellulose, Cotton (for use in explosives)	
Dated			Dec 30, 1976				24 July 1962	24 Aug 1962 (amendment 2 15 nov 1978)	
Classes			Grade A	Grade B	Classification of defect	Method		Class 1	Class 2
Alpha cellulose			95% min	90% min					
Process			Bleached sulfite washed to remove impurities	Bleached sulfite washed to remove impurities					
Species			85% min coniferous	85% min coniferous					
Sampling						UU-P-31 Method 160 or Tappi T414			
Physical properties	Density	g/cm2			Major	UU-P-31 Method 110 or Tappi T411m	Specification for: Inside core diameter, Length of sheets, Width of sheets, Outside roll diameter, Density, Thickness, Weight, Bursting strength		
	Thickness	mm	1.015 max	0.80 min - 1.390 max	Major	UU-P-31 Method 173 or Tappi T411m			
	Weight	g/m2	610.0 min		Major	UU-P-31 Method 110 or Tappi T410m			
Chemical properties	Moisture		10.0 max	10.0 max	Major	UU-P-31 Method 240 or Tappi T412	10.0 max	7.0 max	7.0 max
	Viscosity	cp	10,0 min - 21.8 max	10,0 min - 21.8 max	Major	Tappi T230	140 max	4.4 min - 10.9 max poises	10.0 min - 36.0 max poises
	Alpha cellulose		95.0 min	90.0 min	Major	UU-P-31 Method 201 or Tappi T235	91.0 min		
	Ether extractive		0.20 max	0.40 max	Major	Provided	0.30 max	0.4 max	0.4 max
	Alkali soluble		7.00 max	15.00 max	Major	Provided	10.00 max	5.0 max	5.0 max
	Ash		0.30 max	0.50 max	Major	UU-P-31 Method 202 or Tappi T413	0.30 max	0.5 max	0.5 max
	Lignin						0.40 max		
	Silica						0.008 max		
	Pentosan						6.0 max		
	Lime							Trace	Trace
	Chlorides							Trace	Trace
	Sulfates							Trace	Trace
	Hypochlorities							Trace	Trace
Nitration			Produce Grade A type II NC	Produce Grade B NC	Major		Produce Grade A type II NC and Grade B NC		
Workmanship			Free from oil, grease and other foreign material				Free from dirt, grit, water, oil, grease and other foreign material	Free from foreign material of any kind (such as dirt, oil and stain)	
Absorbancy								Sink below surface in 3 second max	

Summary of canceled cellulose specifications: side by side comparison of main requirements

Standard		Mil-C-216A	Mil-C-2033A	Mil-C-206A
Subject		Cellulose Wood Pulp (Sulfite)	Cellulose, wood pulp (Sulfate)	Cellulose, Cotton (for use in explosives)
Dated		Dec 30, 1976	24 July 1962	24 Aug 1962
Classes		2 (Grade A and B)	1	2 (Viscosity classes)
Species				
Physical properties	Density			
	Thickness			
	Weight			
Chemical properties	Moisture			
	Viscosity			
	Alpha cellulose			
	Ether extractive			
	Alkali soluble			
	Ash			
	Lignin			
	Silica			
	Pentosan			
	Lime			
	Chlorides			
	Sulfates			
	Hypochlorities			
Nitration				
Workmanship				
Absorbancy				

Summary of canceled cellulose specifications: side by side comparison of main requirements

Standard	Mil-C-216A	Mil-C-2033A	Mil-C-206A
Subject	Cellulose Wood Pulp (Sulfite)	Cellulose, wood pulp (Sulfate)	Cellulose, Cotton (for use in explosives)
Dated	Dec 30, 1976	24 July 1962	24 Aug 1962
Classes	2 (Grade A and B)	1	2 (Viscosity classes)
Species			

**Note: Comments
relate to the
perception or
conditions of the
material at the time
the specifications
were created**

-Distinction
between material
to produce Grade
A and Grade B
NC, essentially
related to purity of
cellulose
(Alpha content)

-Species
requirement

-Later addition
-Achieving higher
purity was then
deem more
difficult, however
no distinction
between material
to produce Grade
A and Grade B
NC

No requirement
for species

**-Not specific for
NC**

-Divided in two
classes based on
viscosity

-High purity
material, no
distinction
between Grade A
and B necessary

-No nitration
requirement

Nitration			
Workmanship			

Summary of canceled cellulose specifications: side by side comparison of main requirements

Standard		Mil-C-216A	Mil-C-2033A	Mil-C-206A
Subject		Cellulose Wood Pulp (Sulfite)	Cellulose, wood pulp (Sulfate)	Cellulose, Cotton (for use in explosives)
Dated		Dec 30, 1976	24 July 1962	24 Aug 1962
Physical properties	Density			
	Thickness			
	Weight			



**Note: Comments
relate to the
perception or
conditions of the
material at the time
the specifications
were created**

-Specification only
for fiberboard
characteristics

-Specification for
fiberboard and roll
characteristics :
Inside core
diameter, Length
of sheets, Width
of sheets, Outside
roll diameter,
Density,
Thickness,
Weight, Bursting
strength

Oldest
specification based
on baled cellulose,
does not take into
account fiberboard
cellulose

However...



Absorbancy			
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Summary of canceled cellulose specifications: side by side comparison of main requirements

Standard		Mil-C-216A	Mil-C-2033A	Mil-C-206A
Subject		Cellulose Wood Pulp (Sulfite)	Cellulose, wood pulp (Sulfate)	Cellulose, Cotton (for use in explosives)
Dated		Dec 30, 1976	24 July 1962	24 Aug 1962
Chemical properties	Moisture			
	Viscosity			
	Alpha cellulose			
	Ether extractive			
	Alkali soluble			
	Ash			
	Lignin			
	Silica			
	Pentosan			
	Lime			
	Chlorides			
	Sulfates			
	Hypochlorities			

**Note: Comments relate to
the perception or conditions
of the material at the time
the specifications were
created**

-These are the
core tests for
chemical
characterisation

-A few more tests
required ...

-Lime, Chlorides, Sulfates,
Hypochlorides are useless
for nitration grade
cellulose (Olsen 1929)
-Alpha cellulose was
deemed not necessary
for high purity cotton

Cellulose characteristics: Type 1 and type 2 characteristics

The key characteristics which can affect the performance and processability of cellulose base material are depending not only on the basic chemical characteristics, but also the multi-layered physical structure would requires dividing characteristics in at least 2 groups or types:

Type 1 characteristics: more permanent characteristics not affected by from batch to batch or lot to lot. These characteristics need to be quantify when introducing a new source of cellulose or NC but not for every batch or lot. These characteristics are stable because: rely on essentially one source of raw material, basic nature of processing equipment cannot easily be changed.

In the old days; all NC facility were the same, now several *flavor* of NC can be produced between plants and sometime within one plant,...

Type 2 characteristics: can be affected by normal process variations from batch to batch or lot to lot. (*the good old ones!*)

One important weakness of cellulose and NC specifications: type 1 does not exist, only type 2
Inability to provide a format allowing both types of characteristics.

It also a weakness of NC/propellant industry: not a clear understanding/statement of why characteristics are required (causality)

Where does the effect of a characteristics translate itself in effect in processability and performance along the manufacturing chain *Raw material-Cellulose-NC-Propellant*.

- that knowledge may be considered a technical edge on competition or
- the knowledge was just lost or
- deem too complex or
- ...

Cellulose chemical characteristics: α β γ celluloses

The terms alpha, beta and gamma cellulose are obsolete terms essentially related to solubility fractions of pulp in 18% NaOH.

The old Alkali-soluble test referred to by the cellulose specifications would now be labeled: **S7 @ 100°C**

→ Solubility in 7.14% NaOH @ 100°C

The alpha, beta and gamma cellulose are similar to the combination of more modern R18 and R10 tests.

Alpha cellulose:	Long cellulose (DP>19)	Insoluble 18% NaOH
Beta cellulose	Short cellulose (DP 15-90)	Soluble 18% NaOH
Gamma cellulose:	Hemicellulose (DP<19)	Soluble 18% NaOH

Note: Hemicellulose: mix of 5 (pentoses) and 6 (hexoses) carbon carbohydrates

The S18 portion is pH neutralized and obtaining:

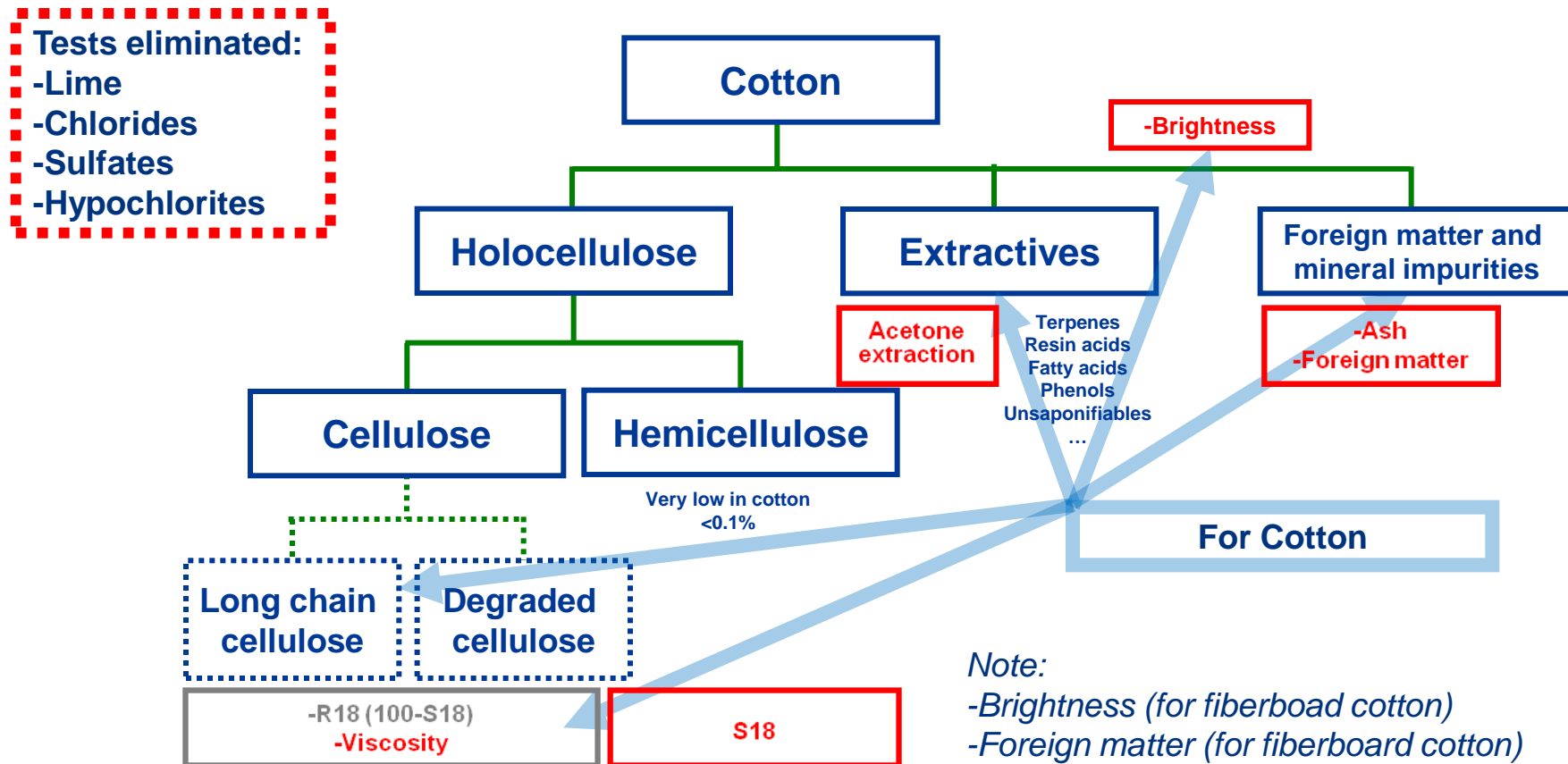
Beta cellulose are insoluble from soluble 18% neutralized

Gamma cellulose are soluble from soluble 18% neutralized

Cellulose chemical characteristics

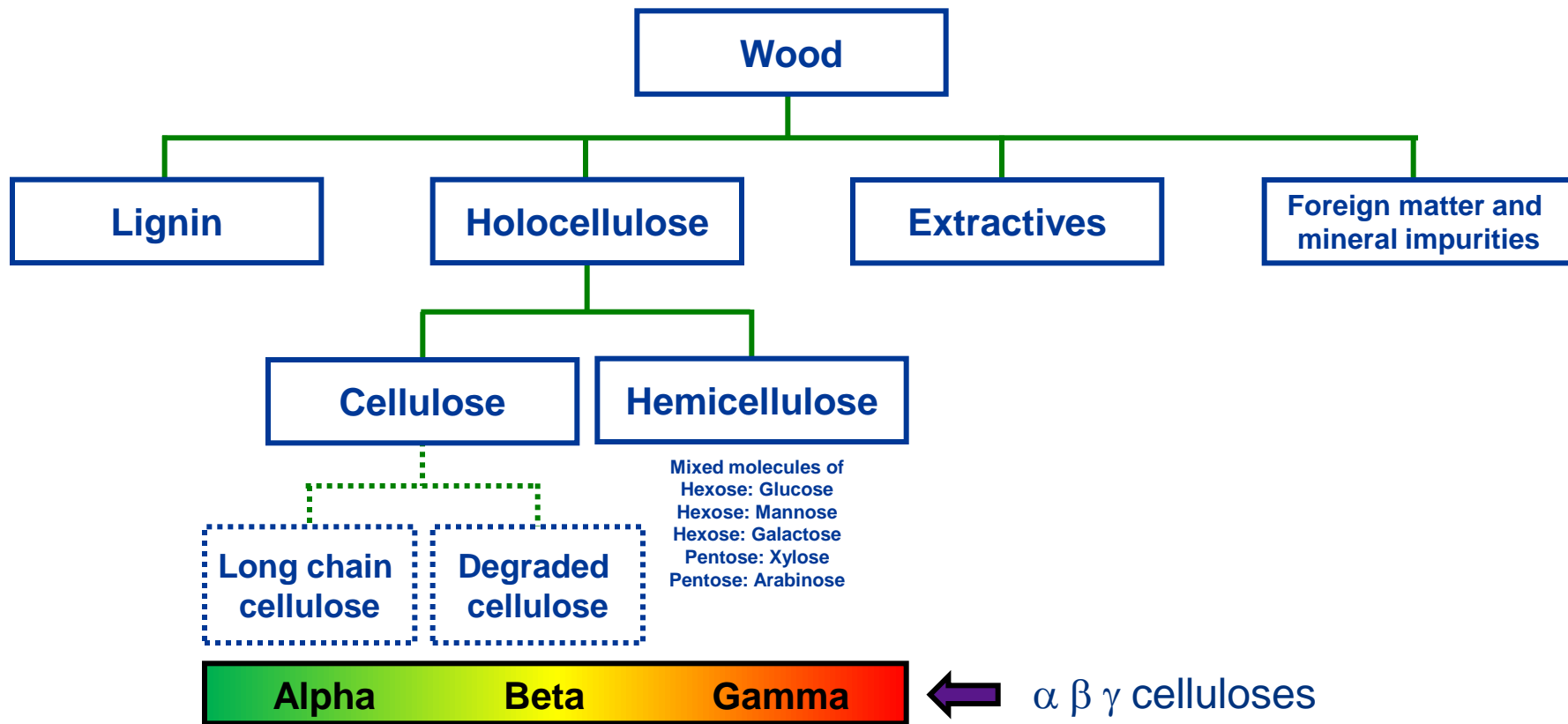
Other tests to be considered (*this list is not exhaustive*):
None

The methods chosen for wood pulp are certainly applicable to cotton



Cellulose chemical characteristics

The division of carbohydrates is summarily defined as:



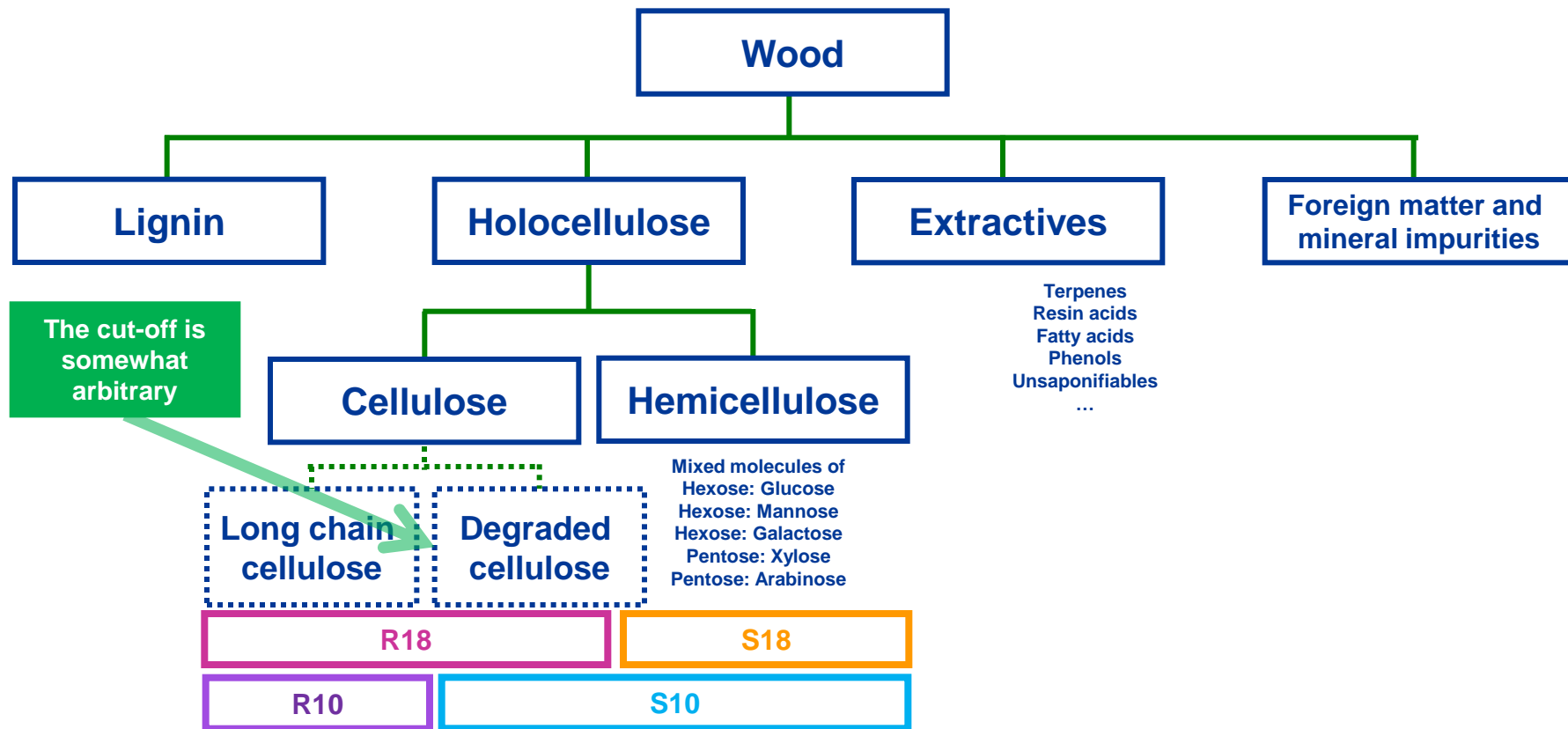
Cellulose chemical characteristics: S18

S18 → Solubility in 18% NaOH @ 20 or 25°C (no significant difference between °C)

From the S18 is calculated the R18 ($100 - S18 = R18$)

R18 → Resistance to 18% NaOH @ 20 or 25°C

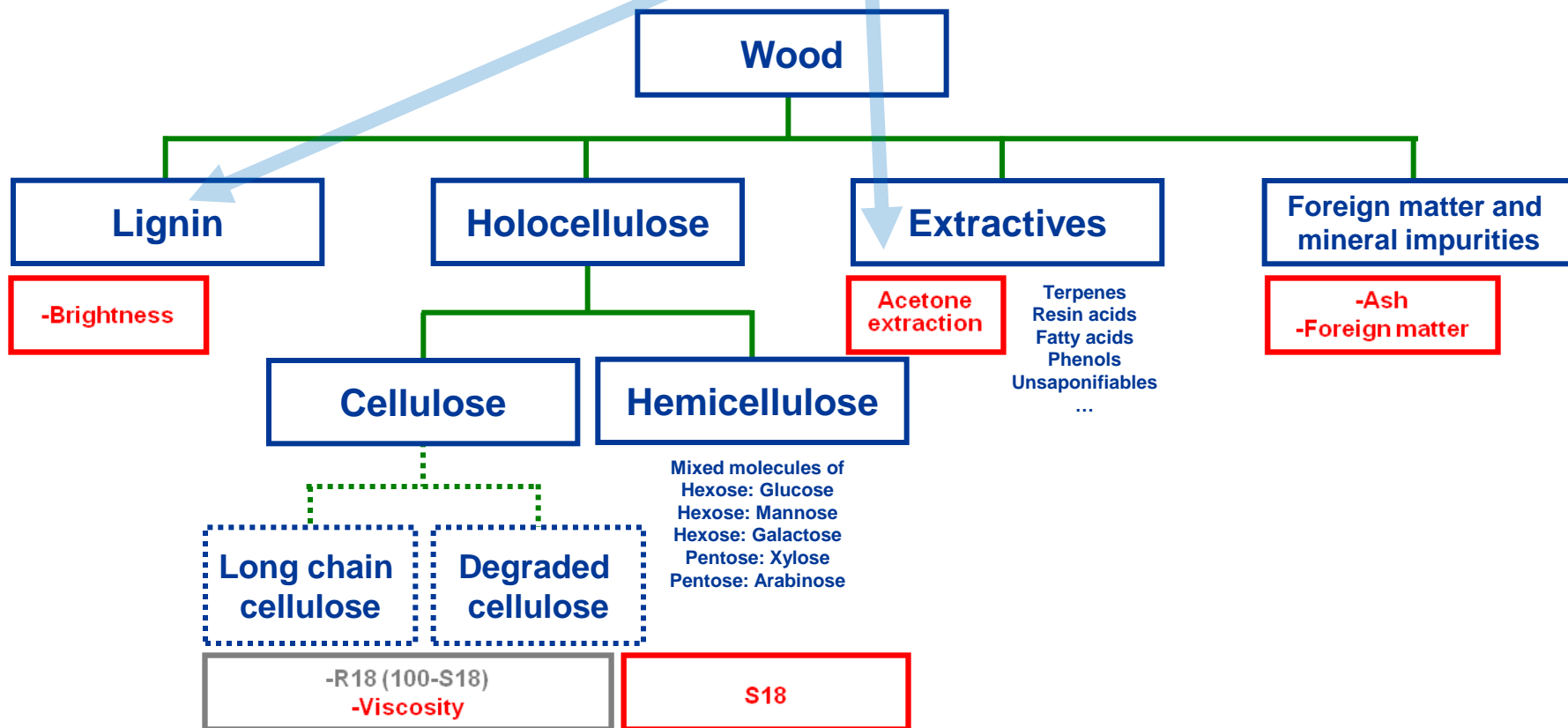
Other S and R are use: S10 R10 are also often encountered



Cellulose chemical characteristics: Impurities

-It is generally recognized that the chromophoric groups on the lignin are principally responsible for colour (also heavy metals and some extractives)

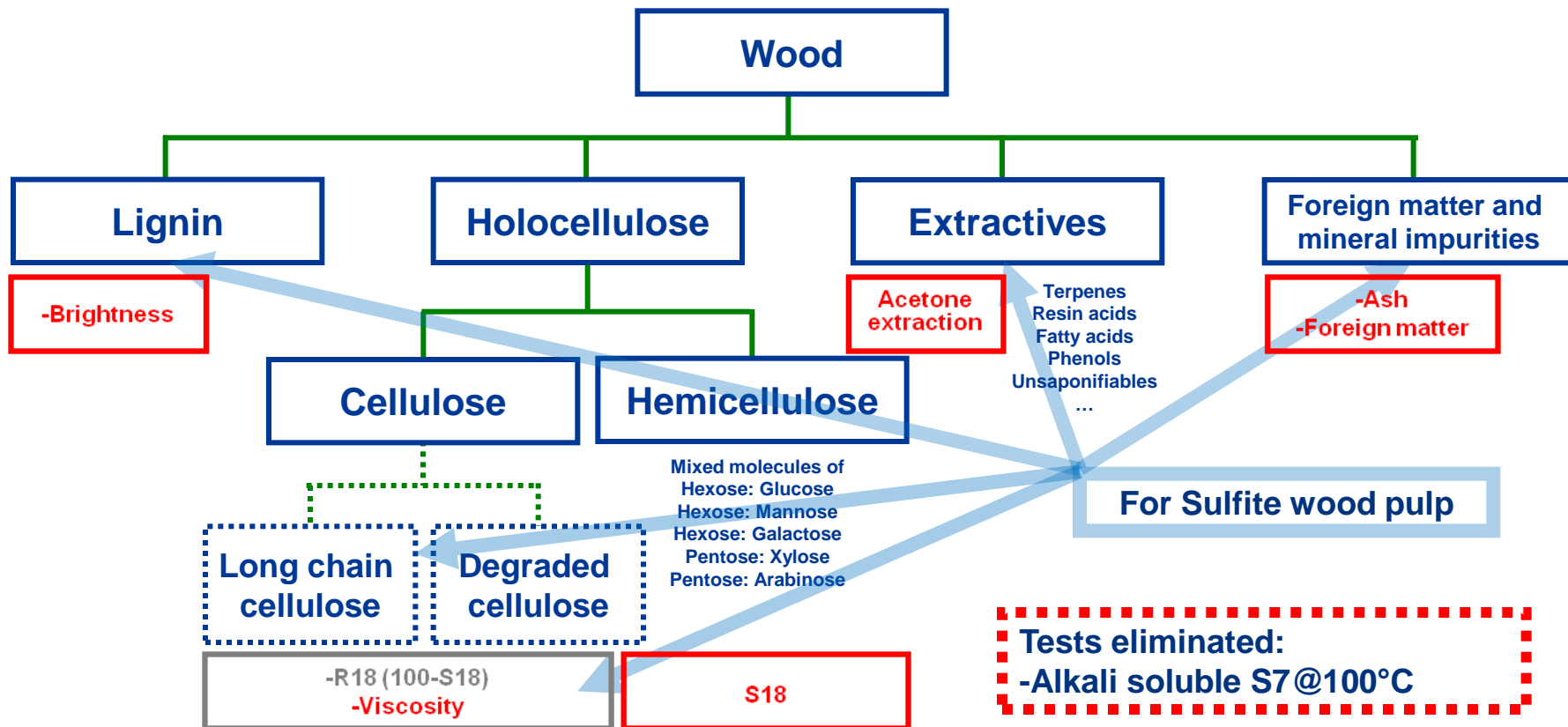
-The ether extraction is replaced by an acetone extraction



Cellulose chemical characteristics: Impurities

Other tests to be considered (*this list is not exhaustive*):

- Drainability test
- Reactivity test
- S10

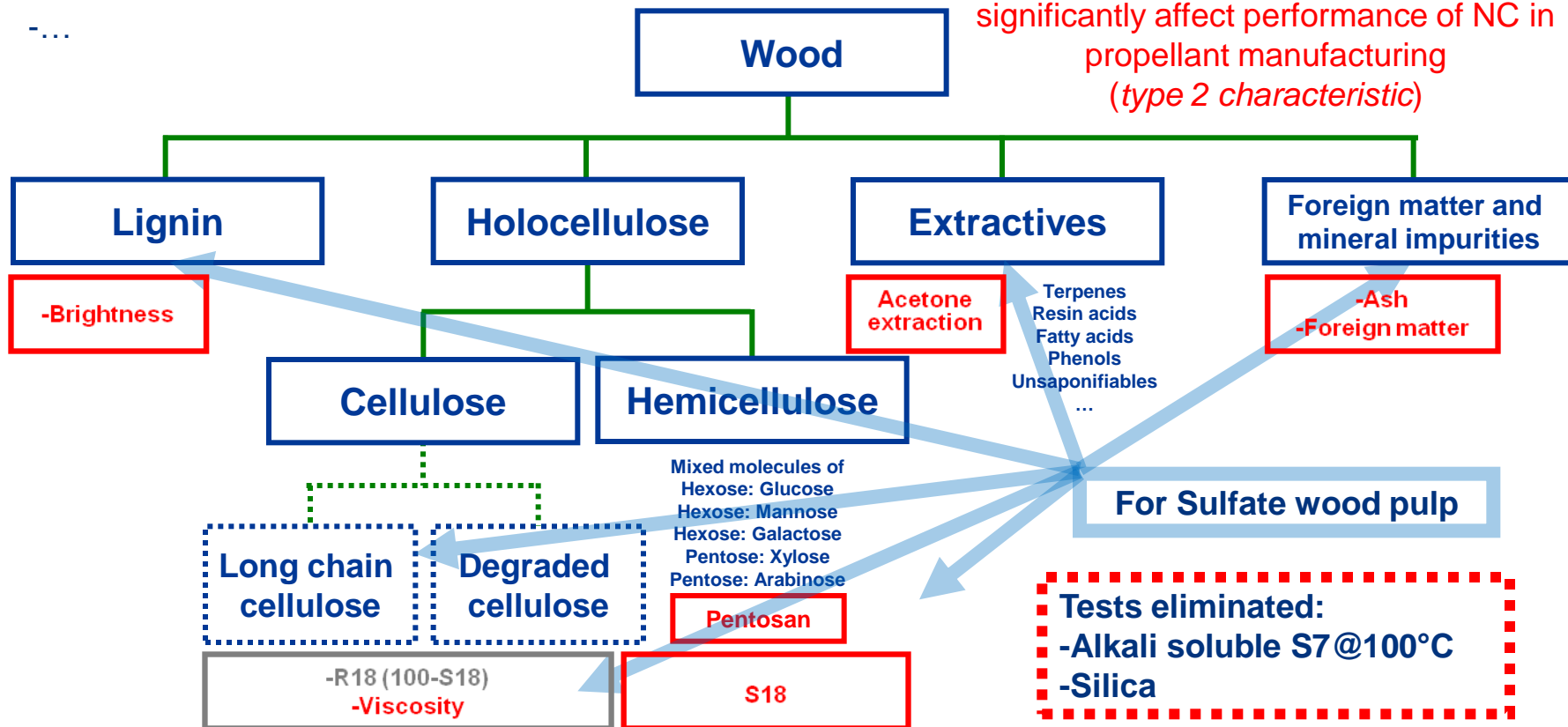


Cellulose chemical characteristics

Other tests to be considered (*this list is not exhaustive*): — ? →

- Drainability test
- Reactivity test
- S10
- ...

Sulfate process introduces the possibility of partial mercerization of cellulose I to cellulose II which can significantly affect nitration quality in ways that it may significantly affect performance of NC in propellant manufacturing (*type 2 characteristic*)



2009 IPT proposed modifications found in original ECP: Applicable to wood and cotton celluloses

Nitration

- The cellulose must successfully be prepared for nitration by milling or cutting to achieve size reduction and increase the accessibility and reactivity of cellulose fibers. It must process satisfactorily to nitrocellulose.
- The cellulose fibers must be resistant and resilient enough to successfully be deflaked and/or refined after nitration.
- Any changes in test methods, chemical and physical properties, and process changes to cooking, bleaching, beating and sheeting processes by the cellulose manufacturer shall be reported to the nitrocellulose manufacturer.

Workmanship

- Examination for workmanship shall be conducted on each sample selected for testing. The cellulose lot shall maintain a uniform composition, texture, and color and be free of foreign matter while meeting all the requirements.
- The cellulose shall be tested using methods as specified in this specification or using at-line /on-line measurement instruments or using equivalent or commercially accepted test methods which shall be reviewed and accepted by the government.
- Equivalent or commercially accepted test methods for cellulose. The nitrocellulose manufacturer will determine the acceptability of an equivalent or commercially accepted test method for cellulose by evaluating if the method is equivalent or correlates with the specified test methods. When the nitrocellulose manufacturer wants to accept an alternate method, government approval must be obtained.

2009 IPT proposed modifications found in original ECP: Applicable to wood celluloses

Cellulose derived from wood.

- The cellulose used shall be derived from wood cellulose obtained by the sulfite process made of bleached sulfite pulp or from wood cellulose obtained by the sulfate process made of bleached sulfate pulp. Only sulfite process wood cellulose shall be used unless approved by the government.
- The cellulose shall be from coniferous woods or a blend of coniferous and broadleaf woods. The bleached sulfite wood cellulose or bleached sulfate wood cellulose shall have been washed to remove purifying chemicals.
- The cellulose shall be fabricated in paperboard form, delivered in rolls or sheets, conforming to the requirements of this specification unless otherwise specified in the contract or purchase order.
- The identification and nominal ratio of wood species from which the paperboard wood cellulose is obtained shall not be modified without approval of the contracting organizations that are acquiring the cellulose and nitrocellulose.

2009 IPT proposed modifications found in original ECP: Applicable to wood celluloses

Physical properties of the wood cellulose fiberboard						
Applicable to	Property	Unit	Specification	Method TAPPI	Method ISO	Note
All wood pulp	Density	g/cm ³	0.84 max	T411	ISO 534	Oven dry basis
All wood pulp	Thickness	mm	1.01 – 1.80	T411	ISO 534	
All wood pulp	Weight	g/m ²	610 minimum	T410	ISO 536	

Fiber morphology and physical properties of wood cellulose fibers						
Applicable to	Property	Unit	Specification	Method TAPPI	Method ISO	Note
All wood pulp	Average fiber coarseness	μg/m	Reported on product description sheet	TAPPI T271	ISO 16065	Including non-polarized light instrument or a commercially accepted test method.
All wood pulp	Fiber length distribution (L _w)	mm				
All wood pulp	Content in fines and short fibers <0.2mm (L _L)	%w/w				

Chemical properties of wood cellulose						
Applicable to	Property	Unit	Specification	Method TAPPI	Method ISO	Note
All wood pulp	Moisture	%w/w	10.0 max	T412	ISO 287	
All wood pulp	Viscosity	cP	10.0 to 22.0	T230		0.5% CED dynamic viscosity
		ml/g	620 to 900		ISO 5351	0.5% CED intrinsic viscosity
All wood pulp	Extractives	%w/w	0.25 max	T280	ISO 14453	Material soluble in acetone
All wood pulp	Alkali solubility of pulp (S18)	%w/w	10.0 max	T235	ISO 692	Solubility in 18% NaOH
All wood pulp	Ash	%w/w	0.25 max	T211	ISO 1762	Ash @ 525°C
All wood pulp	Foreign matter in pulp	mm ² /m ²	100 max	T213	ISO 5350	Dirt in pulp
Specific for sulfite pulp	Brightness of pulp	%	80 min	T452	ISO 2470	
All wood pulp	Content in coniferous and broadleaf woods	Limit: >85% coniferous wood and <15% broadleaf wood				
All wood pulp	Wood species and nominal ratio in pulp	For information only				
Specific for sulfate pulp	Pentosan	%w/w	6.0 max		TAPPI T223	
Specific for sulfate pulp	Lignin	%w/w	0.4% max		TAPPI T222	

2009 IPT proposed modifications found in original ECP: Applicable to cotton celluloses

Physical properties of the cotton cellulose fiberboard					
Property	Unit	Specification	Method TAPPI	Method ISO	Note
Density	g/cm ³	0.374 to 0.851	T411	ISO 534	Oven dry basis
Thickness	mm	0.86 to 1.91	T411	ISO 534	
Weight	g/m ²	493 to 1100	T410	ISO 536	

Chemical properties of cotton cellulose					
Property	Unit	Specification	Method TAPPI	Method ISO	Note
Moisture	%w/w	10.0 max	T412	ISO 287	
Viscosity	cP	12.0 to 32.0	T230		0.5% CED dynamic viscosity
	ml/g	690 to 1400		ISO 5351	0.5% CED intrinsic viscosity
Extractives	%w/w	0.25 max	T280	ISO 14453	Material soluble in acetone
Alkali solubility of pulp (S18)	%w/w	7.0 max	T235	ISO 692	Solubility in 18% NaOH
Ash	%w/w	0.25 max	T211	ISO 1762	Ash @ 525°C
Foreign matter in pulp	mm ² /m ²	15 max	T213	ISO 5350	Dirt in pulp
Brightness of pulp	%	86 min	T452	ISO 2470	

-Cellulose derived from cotton. The material used in manufacture of cotton cellulose shall be bleached cellulose prepared from cotton linters or suitable short-fibered commercial cotton.

-The cellulose can be manufactured in sheeted or baled form.

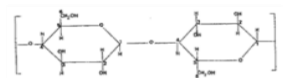
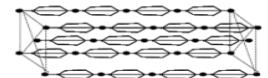
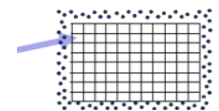
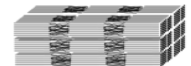
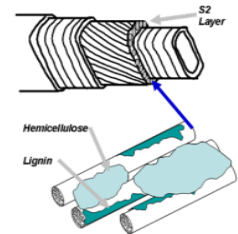
-Only baled cellulose shall be used for combustible cartridge case nitrocellulose unless approved by the government.

Complexity of creating/changing a specification..



Workshop period available to work on this is very time limited, perhaps our expectations from this exercise should be limited to the following:

- Build a basic framework for future discussion
- Inform the community about
 - what has been done so far
 - what is the direction for the future
 - the challenge of revising a specification
- Identify individuals/organization as possible future contributors to the future revisions
- Possible validation of some of the choices relative to the key parameters and analytical methods selected by the IPT in 2009 or, identify people who can help in doing so



Complexity of creating/changing a specification..

- The 2009-2010 revision attempted to cover all types and applications of cellulose combining requirements in one specification.
 - The 2009-2010 specification failed to receive full Government support because trying to cover all types and all applications resulted in very broad ranges of acceptability that basically covered the entire range of the available market (almost all commercially produced cellulose was within the ranges specified in the specification).
 - The US Government wanted more traceability to the source and characteristics of the cellulose used in energetic products.
 - It is generally recognized that identification of the cellulose key characteristics for various end product performance is the most important aspect to capture before beginning other discussions. The cellulose characteristics that contribute to end item performance will then drive the decisions made for the cellulose specifications.
- The knowledge as to why the original cellulose requirements were in place was lost some time ago. It would benefit a great deal if that lost knowledge could be regained, updated, and installed into a modern specification and technical data package.**

